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Effect of the oxygen deficiency on the luminescent properties of the mixed $YV_xP_{1-x}O_4$ phosphors

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In the paper the effect of oxygen vacancies on the luminescent properties of mixed $YV_xP_{1-x}O_4$ phosphors was studied. Amount of oxygen vacancies was controlled by annealing the phosphors in the oxidizing and neutral atmospheres. It was shown that in oxygen-deficient $YV_xP_{1-x}O_4$ phosphors a strong luminescence quenching is observed, which was attributed to the migration-enhanced energy transfer from undistorted to distorted vanadate complexes. Also, the contribution of the emission of such distorted vanadate complexes leads to the broadening and red shift of the luminescence band of the mixed phosphors.

Keywords: orthovanadates, oxygen vacancies, luminescence, quenching.

Вплив дефіциту кисню на люмінесцентні властивості змішаних люмінофорів $YV_xP_{1-x}O_4$. *О.Г.Вягін, І.І.Беспалова, П.О.Максимчук, В.В.Семінько, Е.М.Окрушко, Ю.В.Малюкін.*

Досліджено вплив кисневих вакансій на люмінесцентні властивості змішаних люмінофорів $YV_xP_{1-x}O_4$. Вміст кисневих вакансій контролювався шляхом відпалу люмінофорів в окислювальній і нейтральній атмосферах. Показано, що у дефіцитних за киснем люмінофорах $YV_xP_{1-x}O_4$ спостерігається сильне гасіння люмінесценції, що пояснюється міграційно-посиленим перенесенням енергії від неспотворених до спотворених ванадатних комплексів. Внесок випромінювання таких спотворених ванадатних комплексів приводить також до розширення і червоного зсуву смуги люмінесценції змішаних люмінофорів.

Исследовано влияние кислородных вакансий на люминесцентные свойства смешанных люминофоров $YV_xP_{1-x}O_4$. Количество кислородных вакансий контролировалось путем отжига люминофоров в окислительной и нейтральной атмосферах. Показано, что в дефицитных по кислороду люминофорах $YV_xP_{1-x}O_4$ наблюдается сильное тушение люминесценции, что объясняется миграционно-усиленным переносом энергии от неискаженных к искаженным ванадатным комплексам. Вклад излучения таких искаженных ванадатных комплексов приводит также к уширению и красному смещению полосы люминесценции смешанных люминофоров.

1. Introduction

Orthovanadates of transition and rare earth metals of general formula $MeVO_4$, where Me = Y, La, Gd, Sc, etc. are known luminescent materials. For example, europium-doped yttrium orthovanadates $YVO_4:Eu^{3+}$ are used as red cathodophosphors in color TVs, and neodymium-doped ones ($YVO_4:Nd^{3+}$) as an active media in commercial laser systems [1].

The wide practical use of orthovanadate crystalline host is due to presence of excitation energy migration along the $(VO_4)^{3-}$ vanadate complexes. Such a migration provides an efficient delivery of excitation energy to the luminescence centers (dopant ions). Besides dopant luminescence, the orthovanadate crystals also possess intrinsic host luminescence. The nature of this host luminescence is the so-called charge transfer transitions (CT) in the vanadate complexes. After absorption of a photon, the excited electron transfers from the *p*-orbital of the anion (O^{2-}) to the empty *d*-orbital of the cation (V^{5+}). Charge transfer luminescence of the vanadate complexes is a result of the relaxation of this excited state [2]. However, the presence of energy migration in orthovanadates leads to the strong quenching of the intrinsic luminescence at room temperature due to effective transport of excitations to quenching centers, such as uncontrolled impurities, defects, etc. Therefore, intrinsic luminescence is observed mainly at low temperatures, at which migration is strongly suppressed [3–5].

Nevertheless, in a number of studies was shown [6–8] that weakening the interaction between $(VO_4)^{3-}$ groups by increasing the distance between them allows to observe the CT luminescence of vanadate groups at room temperature. Weakening the interaction may be realized, for instance, for mixed crystals $YV_xP_{1-x}O_4$ or by introducing the $(VO_4)^{3-}$ groups into other compounds. In the case of mixed crystals, the phosphorus ions play the role of energy barriers that spatially limit the migration of excitation allowing controlling the luminescent properties of orthovanadates.

Structural defects also can noticeably affect luminescent processes in crystals. As a rule, in oxide crystals, the main defects are oxygen vacancies. The presence of such vacancies can significantly affect the dynamics of relaxation of electronic excitations in crystals. The study of oxygen defects in the orthovanadate bulk crystals was carried out in a number of works by the optical and EPR methods [9, 10]. It was shown that often the formation of oxygen vacancies in orthovanadates is accompanied by the formation of the V^{4+} ions in the nearest-neighbor sites to the oxygen vacancies [10]. Such a distorted vanadate complex has a wide structureless absorption band with a maximum at about 380–400 nm in the near UV and visible range.

Despite a comprehensive study of orthovanadates, now there are little data on how the formation of oxygen defects affects their luminescent properties. Therefore, in our work, the effect of oxygen vacancies on the luminescent properties of mixed $YV_xP_{1-x}O_4$ phosphors was studied. Amount of oxygen vacancies was controlled by annealing the phosphors in the oxidizing (air) and neutral (argon) atmosphere.

2. Experimental

The mixed $YV_xP_{1-x}O_4$ ($x = 1$; 0.75; 0.5; 0.25; 0.15; 0.05) phosphor powders were obtained by co-precipitation technique. Yttrium chloride hexahydrate $YCl_3 \cdot 6H_2O$ (99.9 %) and anhydrous sodium metavanadate $NaVO_3$ (96 %), orthophosphoric acid H_3PO_4 (85 wt.% in H_2O), sodium hydroxide NaOH (98 %) were acquired from Acros Organics (USA) and used as received.

Suspensions of YVO_4 orthovanadates and YPO_4 orthophosphates were separately prepared. In the case of YVO_4, at the first stage, 0.585 g of ammonium metavanadate NH_4VO_3 was dissolved in the aqueous solution of the sodium hydroxide NaOH ($V = 30$ ml and $C = 0.6$ mol/l), followed by addition 20 ml of distilled water. The pH of the resulting solution of sodium orthovanadate Na_3VO_4 was 12.5–13. A solution of yttrium chloride YCl_3 with $C = 0.5$ mol/l was also prepared by dissolving the weighed quantity of yttrium chloride hexahydrate $YCl_3 \cdot 6H_2O$ in distilled water. Then the solution of Na_3VO_4 in the calculated stoichiometric ratio was added to the solution of YCl_3 and mixed vigorously. The obtained precipitate was washed in distilled water by centrifugation (4000 rpm, 3 min) to obtain the supernatant with pH of 6–7.

In the case of YPO_4, concentrated orthophosphoric acid H_3PO_4 was added dropwise to the YCl_3 solution until the complete precipitation of YPO_4. The obtained precipitate was washed in distilled water by centrifugation (4000 rpm, 3 min) to obtain the supernatant with pH of 6–7.

The resulting suspensions of YVO_4 and YPO_4 were mixed at the temperature of 70–80°C for 5–6 h. Then, the obtained powder samples were annealed at the temperature of 700°C and 1000°C for 2 h and 4 h, respectively. Annealing was carried out both in the air (oxidizing) and argon (neutral) atmosphere in order to varying the content of the oxygen vacancies. Accordingly, in the

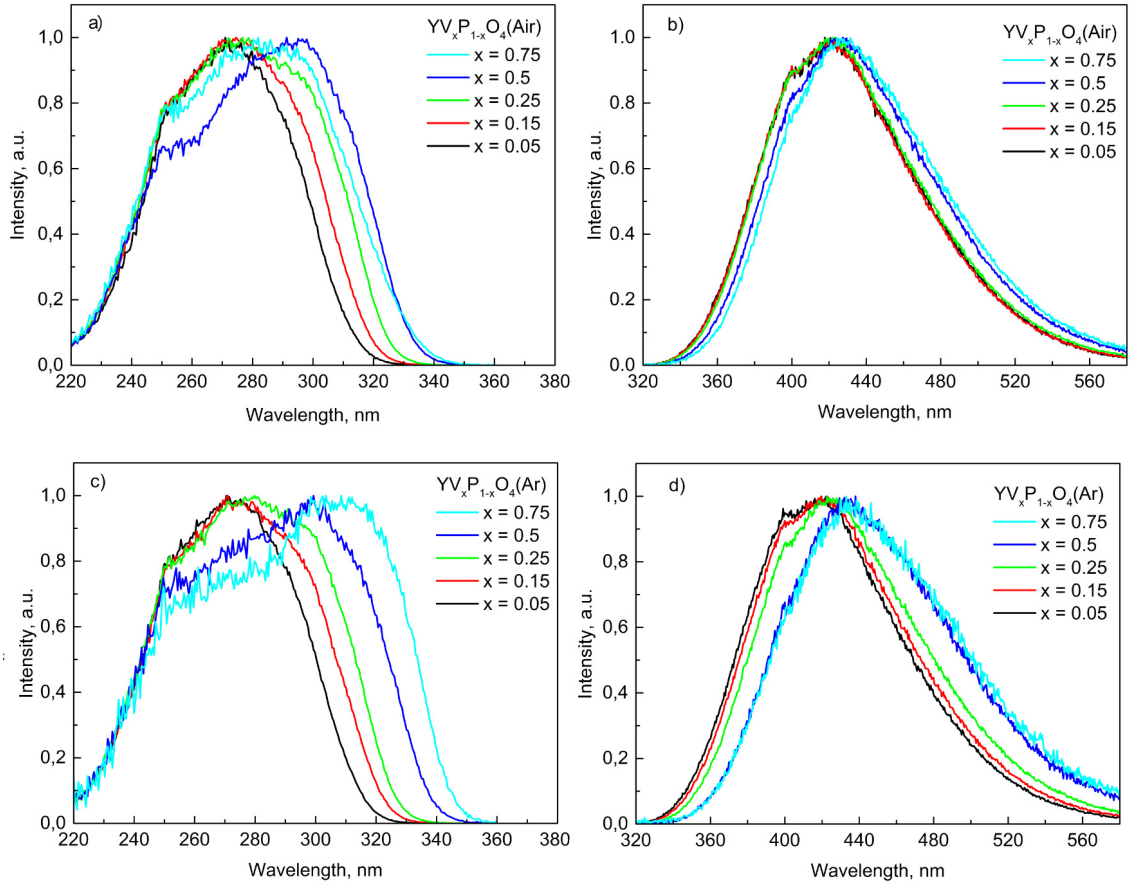

Fig. 1. Normalized excitation and luminescence spectra of the mixed $YV_xP_{1-x}O_4$(Air) (a,b) and $YV_xP_{1-x}O_4$(Ar) phosphors (c,d), λ_{exc} = 300 nm, λ_{reg} = 420 nm.

manuscript text the samples are designated as $YV_xP_{1-x}O_4$(Air) and $YV_xP_{1-x}O_4$(Ar).

The photoluminescence and luminescence excitation spectra were measured using Lumina spectrofluorimeter (ThermoFisher, USA). Both the photoluminescence and excitation spectra were corrected for apparatus response. The luminescence decay curves were obtained by the setup based on the TimeHarp 260 NANO system and the photodetector PMA 182 (PicoQuant, Germany). The samples were excited by the fourth harmonic (266 nm) of YAG:Nd^{3+} pulsed laser (NL202 model, EKSPLA, Lithuania). The grating monochromator was used to select the desired wavelength of the sample luminescence. The average decay times (amplitude weighted) [11] of the samples were estimated by multi-exponential fitting of the decay curves using the FluoFit software (PicoQuant, Germany).

3. Results and discussions

The Fig. 1 shows the normalized excitation and luminescence spectra of the $YV_xP_{1-x}O_4$(Air) and $Y_xP_{1-x}O_4$(Ar) phosphors. As was mentioned above, in orthovanadates the charge transfer takes place between the oxygen ligands and the central vanadium ion. Since significant charge redistribution occurs during such a transition, broad bands with a large Stokes shift (about 11000 cm^{-1}) are observed in spectra.

As the mole fraction (x) of vanadium ions decreases, the excitation and the luminescence spectra of both $YV_xP_{1-x}O_4$(Air) and $YV_xP_{1-x}O_4$(Ar) phosphors shift to the short wavelength range. These phenomena are known for vanadate-phosphate mixed crystals and are associated with a difference in the ionic radii of the cations (in IV-fold coordination, the ionic radii of the V^{5+} ~ 35 pm and P^{5+} ~ 17 pm). Substitution of vanadium ions by smaller phosphorus ones leads to a decrease in the lattice constant and, in turn, to the change of the V–O bond lengths

in the $(VO_4)^{3-}$ vanadate groups [7, 12, 13] leading to the blue shift of the spectra.

For $YV_xP_{1-x}O_4$(Ar) phosphors (Fig. 1c,d), the luminescence and excitation spectra are red-shifted compared to the same bands for the $YV_xP_{1-x}O_4$(Air) by about 5–7 nm (Fig. 1a,b). Also, the spectral width (FWHM) of the luminescence band for the $YV_xP_{1-x}O_4$(Air) phosphors practically does not change when x changes and is about 5500 cm^{-1}. At the same time, the spectral width of the luminescence band for the $YV_xP_{1-x}O_4$(Ar) phosphors monotonically decreases from 5900 cm^{-1} to 5560 cm^{-1} with a decrease in x value (Table). The spectra of the $YV_xP_{1-x}O_4$(Air) did not depend on the excitation wavelength. The spectra of the $YV_xP_{1-x}O_4$(Ar) showed a slight dependence on the excitation wavelength: for instance, upon excitation at the absorption edge at 340–350 nm, the redshift of the luminescence spectra is less than 5 nm. A similar situation is observed for the excitation spectra of the $YV_xP_{1-x}O_4$(Ar) taken at the long-wavelength part of the luminescence bands.

A similar red shift and broadening of the emission band in oxygen-deficient YVO_4 was observed in a number of papers [14, 15] and was attributed to the luminescence of defect VO_4^{3-} complexes, in which one oxygen ion is absent and vanadium ion is reduced to V^{4+}. An analogous phenomenon also was observed in other ABO_4 compounds (where B is W, Mo) [16–19]. Like vanadates, these compounds have a main luminescence band in the blue region of the spectrum associated with the charge transfer in the W^{6+}–O^{2-} and Mo^{6+}–O^{2-} complexes. At the same time, both tungstates and molybdates often show red shift of emission band or additional luminescence bands in the red region which are associated with a distorted tungstate and molybdate complexes with tungsten and molybdenum in the reduced valence state 5+.

Therefore, most likely, the red shift of the luminescence band in the oxygen deficient $YV_xP_{1-x}O_4$(Ar) phosphors is associated to the contribution of the emission of distorted vanadate complex V^{4+}–O^{2-} due to formation of oxygen vacancy and related change in the valence state of a part of V^{5+} ions to V^{4+}. This is also confirmed by the fact that with a decrease in the mole fraction of vanadium ions, the FWHM of the $YV_xP_{1-x}O_4$(Ar) luminescence band also decreases. That is, the number of vanadium ions 5+ which can be reduced to 4+ is decreased.

Table. Dependence of the width (FWHM) of the luminescence band of the mixed $YV_xP_{1-x}O_4$ phosphors on the mole fraction of vanadium ions

Vanadium mole fraction x	FWHM, cm^{-1}	
	$YV_xP_{1-x}O_4$(Air)	$YV_xP_{1-x}O_4$(Ar)
0.75	5560	5895
0.5	5600	5730
0.25	5486	5669
0.15	5452	5589
0.05	5554	5562

As was shown in [15] by means of the theoretical simulation, the presence of oxygen vacancies introduces deep acceptor levels in the electronic structure of YVO_4 that leads to a slight narrowing of its optical gap. This is also consistent with the observed red shift of the excitation spectra in the oxygen-deficient $YV_xP_{1-x}O_4$(Ar) phosphors.

The Fig. 2a shows the dependences of the luminescence intensity of mixed phosphors on the mole fraction of vanadium ions (x). It can be seen that with a decrease in the value of x, the luminescence intensity of the $YV_xP_{1-x}O_4$(Air) increases almost linearly to $x = 0.25$, and then drops. As was mentioned earlier, an increase in the luminescence intensity of vanadate groups with a decrease in their concentration is associated with inhibition of energy migration over such groups, which promotes the quenching of luminescence. Annealing of the phosphors in argon slightly changes this dependence: the total luminescence intensity of the $YV_xP_{1-x}O_4$(Ar) decreases, luminescence rises up more slowly with change the value of x up to x=0.5. After $x = 0.5$ luminescence signal grows faster, but still remains lower than the one for the $YV_xP_{1-x}O_4$(Air).

The overall decrease in luminescence intensity of the $YV_xP_{1-x}O_4$(Ar) may be associated with a decrease in the amount of V^{5+} ions due to partial transition to V^{4+} ones and/or the quenching of luminescence due to a non-radiative transfer of excitation energy to acceptors. It is known that, in the absence of quenching processes, the luminescence intensity increases in direct proportion to the number of emission centers. The luminescence intensity of $YV_xP_{1-x}O_4$(Ar) at the same x values is several times less than that for the $YV_xP_{1-x}O_4$(Air) and the difference between the luminescence intensities for the $YV_xP_{1-x}O_4$(Air) and $YV_xP_{1-x}O_4$(Ar)

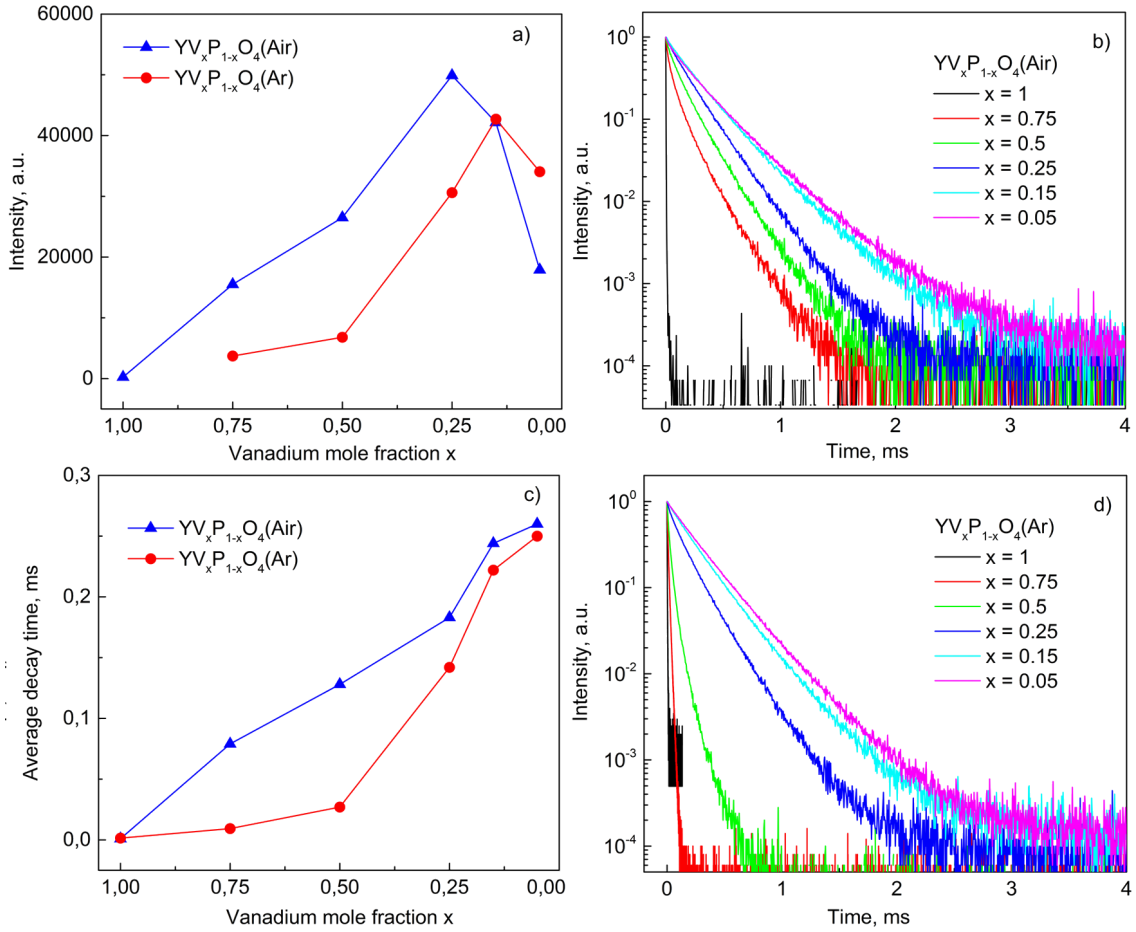

Fig. 2. Dependences of the intensity of the luminescence of the mixed $YV_xP_{1-x}O_4$ phosphors on the mole fraction of the vanadium ions x (a). Photoluminescence decay curves of the mixed $YV_xP_{1-x}O_4$ phosphors after annealing in air (b) and in argon (d), λ_{exc} = 266 nm, λ_{reg} = 420 nm. Dependence of the average photoluminescence decay time of the $YV_xP_{1-x}O_4$ annealed in different atmosphere on the mole fraction of the vanadium ions (c).

varies with x. Under the conditions of our experiment, it is unlikely that such a large part of vanadium ions was reduced to V^{4+}. Therefore, more probably that a decrease in the luminescence intensity in the $YV_xP_{1-x}O_4$(Ar) relative to the $YV_xP_{1-x}O_4$(Air) is due to quenching or energy transfer processes. As was described in Introduction, the absorption band of the distorted vanadate complex with the participation of V^{4+} ions is in the near UV and partly in the visible range and, thus, overlaps with the luminescence band of the undistorted vanadate complexes. So, such distorted complexes can act as energy acceptors for undistorted complexes and quench their luminescence.

To confirm this, the luminescence decay curves of the both $YV_xP_{1-x}O_4$(Air) and $YV_xP_{1-x}O_4$(Ar) phosphors were studied. As can be seen from Fig. 2b,d, for both phosphors, with a decrease in the concentration of vanadium the decay time increases, and at a low concentration of vanadium groups (x = 0.05), when the distance between them is large, the photoluminescence decay curves are almost single-exponential, which, in this case, indicates the absence of migration processes.

Fig. 2c shows the average decay times extracted from the decay curves in Fig. 2b,d. It is seen that the oxygen-deficient $YV_xP_{1-x}O_4$(Ar) phosphors have shorter decay times than that for the $YV_xP_{1-x}O_4$(Air). Also, in the range from x = 1 to x = 0.25 the dependences of decay times on x for the phosphors annealed in different atmospheres differ significantly. For the $YV_xP_{1-x}O_4$(Air), the decay time increases linearly with the x value decrease. For the $YV_xP_{1-x}O_4$(Ar), increasing the decay time of the luminescence of vanadate groups with x value up to x = 0.5 is sufficiently less than for $YV_xP_{1-x}O_4$(Air). In

addition, the difference between the decay times for the $YV_xP_{1-x}O_4$(Air) and $YV_xP_{1-x}O_4$(Ar) decreases with decrease of the x value. In general, this fact correlates very well with the rise up of the luminescence intensity with the decrease in the concentration of vanadium (Fig. 2a).

So, in the oxygen-deficient $YV_xP_{1-x}O_4$(Ar) phosphors, quenching of the luminescence of undistorted vanadate complexes occurs due to energy transfer to distorted vanadate complexes facilitated by migration over undistorted vanadate complexes. Therefore, under conditions of migration, which contribution is still large enough to $x = 0.5$, energy is effectively delivered to such distorted complexes. At $x = 0.25$ and lower, migration is significantly weakened, so the decay time of the $YV_xP_{1-x}O_4$(Ar), as well as its dependence on x, almost does not differ from that for the $YV_xP_{1-x}O_4$(Air).

4. Conclusions

Our experiments show that the formation of oxygen vacancies in the mixed $YV_xP_{1-x}O_4$ phosphors significantly affects their luminescent properties. A strong luminescence quenching in the oxygen-deficient $YV_xP_{1-x}O_4$(Ar) phosphors was found. This quenching was attributed to the migration-enhanced energy transfer from undistorted to distorted vanadate complexes (V^{4+}–O^{2-}). The emission of such complexes leads to the broadening and red shift of the luminescence band of the mixed phosphors. The study of the role of oxygen-related defects in a formation of luminescent properties of orthovanadates of rare-earth and transition metals should allow more effective development of orthovanadate-based luminescent materials.

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